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The Determination of the Crystal Structure of 2-Methyl-2Methylacrylyl-Cyclohexanone- (1,5)-Diaxaspiro Mononeopentyl by X-Ray Christallography

Joann Stevenson

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BY X-RAY CRYSTALLOGRAPHY

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I would like to thank all of my committee members: Dr. John K. Coleman, Chairman of the Department of Physical Science; Professor Philip Schapiro; and Dr. S.N. Rao, Director of Faculty Research at the University of Central Oklahoma; your help has been indispensable. I extend special appreciation to Dr. Joy Flasch, past Director of the Honors Program, for her guidance, support and friendship. Additional thanks go to President Holloway for the privilege of participating in the E. P. McCabe Honors Program and to Dr. JoAnn Clark. To my mother, Bonita L. Stevenson, and my grandmother, Helen Bolton, I love and appreciate your unending support. Anyone omissions are of the mind and not the heart. Above all, I give all praise and thanks to God for every opportunity, blessing, and experience that I have been afforded.

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CHAPTER I

INTRODUCTION

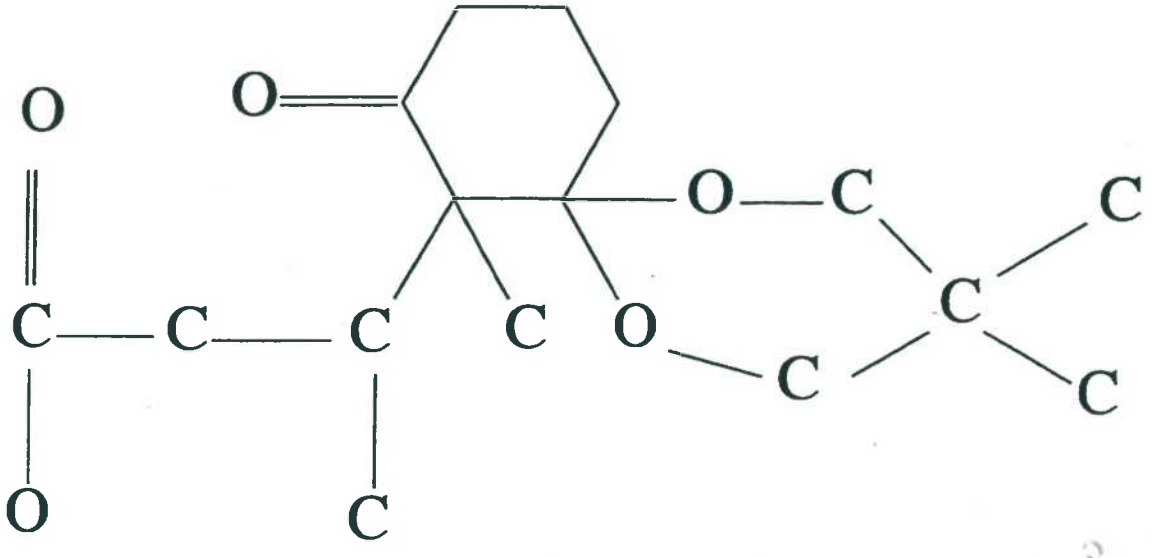
Cyclohexanone

Cyclohexanone, the central component of the compound 2-methyl-2-methylacrylyl-cyclohexanone-(1,5)-diaxaspiro mononeopentyl (see figure on page 2), serves as a solvent for oil in piston type aircraft and in natural and vinyl resins. It is used in the production of crude rubber, waxes, fats, shellac and DDT and other pesticides. Cyclohexanone also is a part of the production of adipic acid, which is used to prepare nylon and is used to prepare cyclohexanone resins via condensation to enhance the adhesive properties of products like floor paints.

Cyclohexanones are among the most accessible hydroaromatic derivatives and serve as the initial materials for the preparation of other compounds. Consequently, their preparation and properties have been extensively studied. The purpose of determining the crystal structure of 2-methyl-2-methylacrylyl-cyclohexanone-(1,5)-diaxaspiro mononeopentyl is to determine the influence of the spiro group on the cyclohexanone conformation and the positions (equatorial or axial) of the methyl and acrylyl groups.

Preparation

Cyclohexanones and subsequent derivatives can be prepared by various methods including the catalytic hydrogenation of phenols and dialkylanilines and the reduction of phenols with lithium dissolved in low-molecular weight amines. They are also prepared by the oxidation



(Fig. 1) Line drawing of the molecule under study

with alkaline permanganate or chromic acid or the catalytic (Cu or Ni) dehydrogenation of cyclohexanols or the oxidation of cyclohexene by reaction with palladium chloride in an aqueous acid.

Properties

Cyclohexanones are most analogous to the aliphatic ketones. They are the simplest of hydroaromatic ketones. They exist as oils, which have a peppermint-like odor, in wood spirits and with their homologues in heavy acetone oils.

Structural Considerations

Substitution of cyclohexanone usually occurs at the 2-methylene groups vicinal to the carbonyl. The most stable conformation (out of boat, twist, chair or twist-boat or twist-chair) is usually the form with the greatest number of substituents in the equatorial positions. The carbonyl oxygen often eclipses the equatorial substituent in the 2 position. The carbonyl on the cyclohexane structure increases ring flatness and flexibility, but the ring maintains the more stable chair conformation.

CHAPTER II

THEORY OF X-RAY DIFFRACTION

X-ray Diffraction

In 1912, Max von Laue discovered that crystals diffract X-rays, proving the wave character of X-rays; no one had characterized their nature since Roentgen's discovery of X-rays in 1895. X-rays lie in the electromagnetic spectrum between ultraviolet light and gamma radiation. The wavelengths of X-rays are about 1.5 to 0.5 Å, which is of the order of atom diameters and, consequently, distances between atoms. The source of the X-rays for diffraction is a rotating anode of copper or molybdenum struck by electrons with energies of 50 keV accelerated by an electron field. 99.3% of the electrons striking the anode produce heat. The anode rotates to disperse this heat. Copper and molybdenum are used because metals with higher atomic numbers have higher scattering powers.

The collisions slow the electrons to produce a continuum of *white radiation*, which is broad-spectrum radiation. A part of the monochromated X-rays passing through the analyte crystals is diffracted (scattered in a forward direction by the atoms) into a detector that gives an image of the diffraction spots. A large number of these images recorded from different crystal orientations are processed into a final list of indexed reflection intensities. The X-rays are diffracted by the crystal at a certain angle. If the wavelength and diffraction angle is known, the interatomic distance, **d**, can be determined by this modification of the Bragg equation ($\lambda=2d\sin\theta$):

$$\mathbf{d=1/2(\lambda \sin \theta)}$$

If the resolution of the image of the diffraction spots is large, **d** can be indistinguishable from the background. Lower resolution, larger θ and lower **d** gives the diffraction image with the detail.

Crystal Systems

A crystal consists of a periodic arrangement of a unit cell, which contains the asymmetric unit (the atom, molecule, etc. that is the structural motif) and its equivalents generated by symmetry. The unit cell is a volume element that may contain the entire repeating motif or parts of several (occurring at the corners or faces of the parallelepiped that is the unit cell). The unit cells builds a 3-dimensional lattice. The lengths of the unit cell edges are *a*, *b*, and *c*, and the angle between *b* and *c* is α, the angle between *a* and *c* is β, and one between *a* and *b* is γ. If one knows the unit cell, the structure can be determined. It is important to choose a primitive unit cell (one having lattice points only at the corners which gives the equivalent of one lattice point per unit cell).

Symmetry occurs from rotation or reflection. Rotation about an axis is indicated as an *n*-fold if rotating 360°/*n* gives and arrangement equivalent to the initial one present. Planes of symmetry, or mirror planes, exist such that every part on one side is related to the other as if reflected. An inversion center occurs where a plane of symmetry intersects an axis of rotation creating a center of symmetry. A combination of a rotation axis and an inversion center creates a rotary inversion axis. The seven primitive crystal lattice systems are designated are shown in the following table. The *n*-fold is designated by an integer; either 1-, 2-, 3-, 4-, or 6-fold axes can occur in normal crystals. The letter *m* indicates the mirror plane and a bar over an integer indicates a rotary inversion axis or center.

The Seven Crystal Systems

Crystal System	Number of Independent Parameters	Parameters	Lattice Symmetry
Triclinic	6	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$	1
Monoclinic	4	$a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta > 90°$	2/ *m*
Orthorhombic	3	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	*mmm*
Tetragonal	2	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	4/ *mmm*
Trigonal			
rhombohedral lattice	2	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$	3 *m*
hexagonal lattice	2	$a = b = c$; $\alpha = \beta = 90°$; $\gamma = 120°$	6/ *mmm*
Hexagonal	2	$a = b = c$; $\alpha = \beta = 90°$; $\gamma = 120°$	6/ *mmm*
Cubic	1	$a = b = c$; $\alpha = \beta = \gamma = 90°$	*m*3*m*

These seven primitive lattices are designated by a **P** placed before the symmetry symbol. Bravais discovered seven more nonprimitive lattices that contain two or more lattice points per unit cell. They are viewed as combination of a primitive lattice with one or more offset copies of itself. The letters **A**, **B**, or **C** precede the symmetry symbol for face-centered cells, **I** for body-centered cells, and **F** for cells with all faces with centered lattice points.

Crystals are then classified by the group of symmetry operations relating their faces. These point groups represent the unique combinations of the symmetry elements found in the primitive lattice systems. The faces represent the planes that define the solid figure of the crystal. There are 32 unique point groups divided among the seven crystal systems. The faces that develop from crystal growth are a direct result of the arrangement of the asymmetric unit and ideally conform to one of the 32 point groups.

Combining the 32 point groups with the 14 Bravais lattices leads to the 230 unique space groups that describe the only ways that identical object can be arranged in an infinite lattice. The additional symmetry elements in space groups combine translation along an axis with rotation or reflection. Combining a rotary axis and a translation produces a screw axis. Combining a

translation and a mirror plane produces a glide plane. A space group designation includes the capital letter indicating the lattice type followed by the point group symbols with rotation and reflection symmetry elements extended to indicate screw axes and glide planes. The space group for 2-methyl-2-methylacrylyl-cyclohexanone-(1,5)-diaxaspiro mononeopentyl is $P2_1/c$ indicates a primitive unit cell with a 2-fold screw axis translated 1/2 of the unit translation with a glide plane parallel to the c-axis. If the space group is known, calculations are reduced because symmetry reduces the number of reflections that must be collected.

Reciprocal Lattice

The reciprocal lattice has dimensions that are reciprocal to the original cell and correspond to the positions of the reflections. The size of the reciprocal lattice indicates the intensity of the reflection and corresponds to the contents of the unit cell. Each point of the reciprocal lattice corresponds to the diffraction from a periodic set of specific crystal lattice planes defined by the index triple *hkl*. The relationship between the direct and reciprocal lattices depends on the angles between the axes in the direct lattice. The axes in the reciprocal lattice are designated a^*, b^*, and c^* and the angles are α^*, β^*, and γ^*. The relationship between the direct and reciprocal lattice in a general oblique system is

$$a^* = \frac{bc \sin \alpha}{V} \qquad a = \frac{b^*c^* \sin \alpha}{V^*} \qquad V = 1 / V^*$$

$$b^* = \frac{ac \sin \beta}{V} \qquad b = \frac{a^*c^* \sin \beta}{V^*}$$

$$c^* = \frac{ab \sin \gamma}{V} \qquad c = \frac{a^*c^* \sin \gamma}{V^*}.$$

In an orthorhombic system the relationship is simplified to

$a = 1 / a^*$ $b = 1 / b^*$ $c = 1 / c^*$ $\alpha = \beta = \gamma = \alpha^* = \beta^* = \gamma^* = 90°$

$V^* = 1 / V = a^* b^* c^*$ $V = 1 / V^* = abc$.

The vector v(*hkl*) is from the origin to the lattice point (h, k, l).

Scattering Factors

When the incoming rays are scattered forward, the scattering power will depend on the number electrons in the particular atom. For neutrons of the same wavelength, the scattering factor is not angle determined because the atomic nucleus is odors of magnitude smaller than the electron cloud. The scattering power of an atom will decrease with the scattering angle and increase for heavier atoms as shown by a plot of scattering factor f in units of electrons vs. $\sin\theta/\lambda$. For $\theta = 0$, f equals the number of electrons. The scattering factor for an atom i at any scattering angle is

$$f°(\sin\theta/\lambda) = \sum_{i=1}^{4} \mathbf{a}_i \cdot e^{-bi(\sin\theta/\lambda)^2} + \mathbf{c}\,.$$

However, the scattering factor contains additional complex contributions from anomalous dispersion. If the frequency of the incident beam falls near the natural frequency of some atom type, an anomalous phase change occurs on the scattering by atom of that type. Their contributions can be computed and used to determine phases. The scattering factors become

$$f = f° + f' + i \cdot f''$$

where f' is a real correction term and f'' is the imaginary term.

There is a positive 90° phase shift between the real and imaginary components of the corrected scattering factor. The temperature, **B-**, or Debye-Waller factor also weakens the scattering power of atoms. The magnitude of the perpetual vibrations of atoms about their

resting points generally increases with temperature. This thermal motion spreads electron clouds over larger volumes and causes a steeper attenuation in the scattering power of a real atom relative to an ideal stationary one. This exponential factor corrects the structure factor as follows:

$$f_B = f \cdot e^{-B(\sin\theta/\lambda)^2}.$$

where $\mathbf{B}=8\pi^2\langle u\rangle^2$; $\langle u\rangle$ is the mean displacement of a vibrating atom.

Isotropic average displacement assumes all atoms are vibrating with the same amplitude and the motions are symmetric. Anisotropic (hydrogen) displacement does not assume symmetric spherical motion and the single thermal parameter is replaced by six of them that describe the size and orientation of the vibration ellipsoid.

Structure Factors

The individual atomic scattering factors (f_j) are used to calculate the structure factors:

$$\mathbf{F_{(h,k,l)}}=\sum_{j=1}^{atoms} f_j \exp[\, 2\pi \cdot i\, (\mathbf{hx_{(j)}} + \mathbf{ky_{(j)}} + \mathbf{lz_{(j)}})]$$

which is directly related to the intensity, I_{hkl}, of the reflection indexed *hkl*:

$$\mathbf{I_{hkl}} = |\, \mathbf{F_{hkl}}\, |^2 \cdot \mathbf{Lp} \cdot \mathbf{A}\,.$$

Lp is the geometry (Lorenz) and polarization factor dependent on the experimental setup and accounted for early in data processing. **A** is an optical absorption correction factor. **F** cannot be calculated from the intensity, only its scalar magnitude. Because only diffraction magnitudes are collected, not their phases (which contain the bulk of the structural information), solving the phase problem becomes the major challenge of structure solutions.

Fourier Transforms

The structure factors can be used as Fourier coefficients in a Fourier synthesis (summation) to generate electron densities:

$$\rho_{(x,y,z)} = 1/V \sum_{h}\sum_{k}\sum_{l} \mathbf{F}_{(h,k,l)} \exp\,[-2\pi \cdot i\,(hx + ky + lz)].$$

The extent to which the diffraction pattern is observed causes real limitations (completion requires summation from negative to positive infinity). The synthesis is approximate and may show truncating affects. This equation indicates that the electron density is the *Fourier transform* of the structure factors. A Fourier transform is a representation of a function in terms of a set of sine waves. The set of different frequencies is orthogonal, and any continuous function can be represented by summing enough sine waves of the appropriate frequency amplitude and phase. After determining the atomic scattering factors and using a structure solution to determine the phase angle of the reflections, the structure factors can be calculated and used in a Fourier synthesis to generate electron density maps which are used to hypothesize atom locations.

CHAPTER III

EXPERIMENTAL SETUP

Diffractometer

The first component of the X-ray diffraction experimental setup is the X-ray tube, which consists of an electron source and metal anode that emits X-rays. The less expensive, more common hot cathode tube has electrons liberated from a heated filament and accelerated through a high potential towards the anode target. These permanently sealed have 5,000-10,000 hour working lives but tend to become "dirty' and emit spurious radiation with area and are restricted to a single anode material. Rotary anode tubes are expensive, complicated, and difficult to maintain but are considered relatively trouble-free in terms of data quality and are commonly used. This tube can sustain 10 or more times the power of one with stationary anodes.

The primary X-ray beam is focused to a single wavelength by focusing a mirror a crystal monochromator and passed through a collimator, which makes the paths of radiation parallel. The collimated X-rays pass through a crystal mounted on a four-circle goniometer, which consists of a pin to hold the crystal on the goniometer head and some variant of the four-circle diffractometer. These arcs (circles) are the crystal orienter, which contains the phi (ϕ) and chi (χ) circles and the base containing the omega (ω) and two-theta (2θ) circles. The arcs are used to adjust the crystal and counter (detector) orientation to collect desired planes of reflection. The diffracted X-rays are recorded by a detector or precision camera that maps one reciprocal

lattice level onto one sheet of film from which the angles and distances can be measured and data can be indexed.

Structure Determination

The raw intensity data is imputed into a structured determination program to be reduced. Absorption corrections may be complex and are made least often. These rigorous calculations involve determining the absorption for the path length through the crystal by the beam reflecting from each tiny part of the crystal and integrating over the entire volume of the crystal. Molybdenum radiation generally renders these corrections less significant, but determining the effect of the rays traversing the minimum and maximum crystal dimensions can estimate the magnitude of the problem. Crystal decay is shown when standard reflections are measured repeatedly at regular intervals. This decay is generally random, due mostly to radiation damage, and differs considerably among reflections. To minimize errors from large and random fluctuations in decay approximations, the crystal is often "cryo-cooled" or flash-cooled to cryogenic temperatures which also reduces the overall temperature factor.

The relationship between observed structure factors and the experimentally observed intensities is expressed by

$$|\mathbf{F}_{hkl}|=(\mathbf{K}\mathbf{I}_{hkl}/\mathbf{L}\mathbf{p})^{1/2}$$

The variable **p** is the polarization factor given by

$$\mathbf{P}=\frac{\mathbf{1}+\mathbf{K}\cos^2 2\theta}{\mathbf{1}+\mathbf{K}}$$

when using a crystal monochromator. The Lorentz factor, **L**, depends on the precision of the measurement technique and is given by

$$L = \frac{\sin\theta}{\sin 2\theta(\sin^2\theta - \sin^2\theta)^{1/2}}$$

The term **k** depends on crystal size, beam intensity, and some fundamental constants. The polarization term occurs because the X-ray beam is initially unpolarized and the reflection efficiency varies with the reflection angle. The Lorentz factor comes from the time required for a point to pass through a sphere of reflection which varies with its position in reciprocal space and the direction with which it approaches the sphere.

The average observed intensity with Lorentz and polarization effects is

$$\bar{I}_{rel} = \langle |F_{rel}|^2 \rangle_{ave}$$

and for a unit cell that has **N** atoms, the theoretical average intensity is

$$I_{obs} = \sum_{i=1}^{N} f_i^2$$

It depends on cell constants. Normal organic crystals generally provide ~100-150 unique reflections per nonhydrogen atom (×10 for molybdenum radiation), and 4 or 5 reflections are taken for each adjustable parameter. The reflections are averaged to reduce the data set. The data are weighted at various stages in terms of their estimated reliability and the degree to which they differ from those predicted by the current model.

The phases of the reflections are determined from the reduced data set. Direct methods include inequalities from the combination of structure factor expressions and certain classical inequalities. Structure invariants, phase combinations that do not change with arbitrary assignment of cell origins, and semi-invariants, which do not change with shifts in origin have a symmetry that can be used to determine phases. Other direct methods include the multiple tangent solution and centrosymmetric and noncentrosymmetric probability methods. The

indirect Patterson method was the major method of the past. It involves locating a heavy atom by using a map form the square of the structure factor magnitudes to find interatomic vectors. Heavy atom peaks stand out sharply against the background of lighter atom vectors due to weighting. The trial structure is refined by a Fourier synthesis, locating hydrogen atoms, and least squares (the refinement of assumed structure factors vs. observed).

My Experimental Data

My experiment used an Enraf-Nonius CAD4 diffractometer with molybdenum radiation with a wavelength of 0.71073 Å and a graphite crystal monochromator. Additional experimental data is given by the output on the following pages processed by the Frenz Personal Structure Determination Program (SDP) on a 386sx/16 computer. Twenty-five (25) reflections were taken for cell measurements in the theta (θ) range of 4-20° at a temperature of 293 K. the crystal color was transparent; its shape was rectangular, and it measured 0.35 mm × 0.28 mm × 0.12 mm. The density calculated from independent measurements was 1.25 g/cm^3. The formula weight of the compound ($C_{16}H_{24}O_5$) is 296.36 g/mol. The crystal was monoclinic and the space group was $P2_1/c$. There were four (4) formula units per unit cell. The unit cell had dimensions of 13.049Å for *a*, 10.411 Å for *b*, and 12.317 Å for *c*. The α,β. And γ angles were 90.0°, 105.5°, and 90.0°, respectively. 3244 reflections were measured by the omega (ω) method at a rate of 1-10/min.; 3009 were unique. The symmetry of the reciprocal lattice causes reflections with related indices to have the same intensities, and only one member of the set needs to be measured—the unique data set. Three (3) standard reflections were monitored every 100 reflections to observe intensity decay or movement of the crystal. The variations in the intensities can indicate working precision, systematic errors in the equipment, or crystal changes. If the changes are relatively

small (<20% of the total intensity), accuracy can be obtained by using the standard reflections to define a normalization curve to give reflections measured at different times a common basis.

The cell was refined by the least squares method. Lorentz and polarization corrections were applied along with a secondary extinction correction to reduce the data. No absorption correction was made. The structure was solved by the semi-invariant representation (SIR) method. Hydrogen atoms were found by difference Fourier.

a	13.049 (0)
b	10.411 (0)
c	12.317 (0)
Ã	105.46 (0) ½
V	1612.8 3
Z	4
Dcalc	1.22 g/cm3
Radiation	Mo KÁ (0.71073)
Ì	0.8 cm-1
F(000)	640
Temperature	0 þ 1½
Unweighted agreement factor	0.055
No. of reflections measured	3244 total, 3009 unique

Acta Cryst. C - Tables

Chemical name	[ENTER COMPOUND NAM
Chemical name	E]
Formula weight	296.37
System	monoclinic
Space group	# 0 P12(1)/c1
a	13.049 (0)
b	10.411 (0)
c	12.317 (0)
Ã	105.46 (0) ½
V	1612.8 3
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Table of Experimental Details
1. Crystal Data

Crystal color	[ENTER COLOR]
Crystal shape	[ENTER SHAPE]
Crystal dimensions	0.00 x 0.00 x 0.00 mm
Instrument	Enraf-Nonius CAD4 diffractometer
Corrections	Lorentz-polarization
	reflection averaging (agreement on I = 1.8%)
Maximum 2Õ	72.9½
h data range	-15 to 14
k data range	-12 to 0
l data range	0 to 14
Number unobserved data	1308

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k data range	-12 to 0
l data range	0 to 14
Number unobserved data	1308
Reflections included	1701 with Fo»>3.0Í(Fo»)

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Table of Experimental Details
B. Intensity Measurements

Instrument	Enraf-Nonius CAD4 diffractometer
Monochromator	graphite crystal, incident beam
Attenuator	Zr foil, factor 12.2
Detector aperture	1.8 to 5.9 mm horizontal 4.0 mm vertical
Scan type	w-Õ
Scan rate	1 -10½/min (in omega)
Scan width, deg	0.9 + 1.500 tan Õ

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Table of Experimental Details
C. Structure Solution and Refinement

Anomalous dispersion	all non-hydrogen atoms
Parameters refined	190
Unweighted agreement factor	0.055
Weighted agreement factor	0.071
Factor including unobs. data	0.168
Esd of obs. of unit weight	2.30
Convergence, largest shift	1.02Í
Refinement	full-matrix least-squares
Minimization function	õw(|Fo|-|Fc|)»
Least-squares weights	4Fo»/Í»(Fo»)
High peak in final diff. map	0.66 (11) e/3
Computer hardware	386SX/16
Computer software	Personal SDP
	B. A. Frenz & Associates, Inc.

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-squares weights	4Fo»/Í»(Fo»)

CHAPTER IV

RESULTS

1701 reflections were refined by 190 parameters using the full-matrix least-squares method to converge with an unweighted agreement factor(R) of 0.055 (5.5%) and a weighted agreement factor (wR) of 0.071 (7.1%). The agreement factor including unobserved data was 0.168 (16.8%). The largest shift in conversion was 1.02. The cyclohexanone ring is in a chair conformation. The methyl group is in the axial position, and the acrylyl group is equatorial. The dihedral angle between the two mean ring planes is 73°. The spiro carbon is surrounded bond angles from 104.8-113.0° indicating that it is tetrahedral. The highest peak in the final difference Fourier map had a height of 0.66 e/A with an estimated error of 0.11. Graphs of $w(|F_O| - |F_C|)$, reflection order in data collection, sin θ/λ, and other indices showed no unusual trends. The maximum sin θ/λ was 0.5941. The maximum F_O was 225.42 with a scale factor of 0.2503. The estimated standard deviation of the observation of unit weight was 0.79. The linear absorption coefficient (μ) was 0.06 mm. The density calculated from the formula unit cell was 1.22 g/cm^3. The observed intensity (crystal) decay was <5%. The following tables give positional parameters and their estimated standard deviations, general anisotropic displacement parameter expressions (**B**'s and **U**'s), torsion angles in degrees, and statistics based on data collection order and magnitude of F_O. Tables of structure factors, hydrogen atom coordinates, and bond distance and angles involving hydrogen atoms are also supplied. There are plots of parity groups, weighting scheme analysis, magnitude of F_O and statistics based on indices.

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A»)
O1	0.3788(2)	0.5576(2)	0.0191(2)	5.52(6)
O2	0.5013(2)	0.6482(2)	-0.0485(2)	4.27(5)
O3	0.3043(2)	0.7026(2)	-0.2997(2)	5.85(6)
O4	0.3355(1)	1.0401(2)	-0.3693(1)	3.50(5)
O5	0.3799(1)	1.1321(2)	-0.1899(1)	3.33(4)
C1	0.4176(2)	0.6546(3)	-0.0209(2)	3.34(7)
C2	0.3587(2)	0.7782(3)	-0.0281(2)	3.21(7)
C3	0.2803(3)	0.7861(4)	0.0221(3)	5.24(9)
C4	0.3966(2)	0.8907(3)	-0.0836(2)	3.15(7)
C5	0.3460(2)	0.9071(3)	-0.2123(2)	2.86(6)
C6	0.2257(2)	0.9233(3)	-0.2340(3)	3.97(8)
C7	0.3696(2)	0.7867(3)	-0.2738(2)	3.61(7)
C8	0.4782(3)	0.7725(3)	-0.2936(3)	4.77(8)
C9	0.5265(2)	0.8943(3)	-0.3253(3)	4.77(8)
C10	0.5136(2)	1.0061(3)	-0.2496(3)	4.00(7)
C11	0.3956(2)	1.0254(3)	-0.2555(2)	2.88(6)
C12	0.3565(3)	1.1564(3)	-0.4215(3)	4.18(7)
C13	0.3379(3)	1.2739(3)	-0.3548(3)	4.31(8)
C14	0.3797(4)	1.3944(4)	-0.4013(3)	6.8(1)
C15	0.2209(3)	1.2883(4)	-0.3619(3)	6.8(1)
C16	0.4016(3)	1.2545(3)	-0.2341(3)	4.19(8)
H1	0.227	0.724	-0.006	6.67
H2	0.308	0.775	0.102	6.67
H3	0.473	0.709	-0.353	5.51

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A»)
H4	0.527	0.739	-0.227	5.51
H5	0.490	0.915	-0.404	5.91
H6	0.600	0.881	-0.323	5.91
H7	0.555	0.992	-0.175	5.17
H8	0.541	1.086	-0.275	5.17
H9	0.310	1.161	-0.497	5.41
H10	0.428	1.156	-0.428	5.41
H11	0.344	1.410	-0.477	8.56
H12	0.375	1.469	-0.357	8.56
H13	0.456	1.385	-0.397	8.56
H14	0.180	1.299	-0.440	8.92
H15	0.195	1.213	-0.334	8.92
H16	0.208	1.360	-0.320	8.92
H17	0.477	1.261	-0.227	5.47
H18	0.385	1.322	-0.187	5.47
H19	0.211	0.999	-0.196	5.03
H20	0.193	0.932	-0.312	5.03
H21	0.196	0.852	-0.206	5.03
H22	0.472	0.882	-0.072	3.91
H23	0.384	0.968	-0.047	3.91
H24	0.295	0.777	-0.088	3.96
H25	0.351	0.486	0.051	6.67
H26	0.249	0.871	0.010	6.67

Parameters without esd's were not refined.
Anisotropically refined atoms are given in the form of the

isotropic equivalent displacement parameter defined as:
(4/3) * [a»*Ã(1,1) + b»*Ã(2,2) + c»*Ã(3,3) + ab(cos Ó)*Ã(1,2)
+ ac(cos Ã)*Ã(1,3) + bc(cos Á)*Ã(2,3)]

Table of General Displacement Parameter Expressions - B's

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
O1	5.34(9)	3.4(1)	9.1(1)	-0.13(8)	4.12(8)	1.92(9)
O2	3.80(8)	3.8(1)	5.82(9)	0.52(8)	2.34(7)	1.32(9)
O3	5.5(1)	4.7(1)	7.2(1)	-1.3(1)	1.30(9)	-2.5(1)
O4	3.91(8)	3.9(1)	2.58(7)	0.48(8)	0.75(6)	0.02(8)
O5	4.62(8)	2.77(8)	2.73(7)	0.09(8)	1.19(6)	-0.11(7)
C1	3.3(1)	3.2(1)	3.7(1)	-0.3(1)	1.14(9)	0.1(1)
C2	3.0(1)	3.6(1)	2.9(1)	0.1(1)	0.58(9)	0.3(1)
C3	5.2(2)	5.6(2)	5.5(2)	1.3(1)	2.4(1)	1.1(2)
C4	3.4(1)	2.9(1)	3.0(1)	-0.1(1)	0.6(1)	-0.1(1)
C5	2.8(1)	3.0(1)	2.8(1)	0.0(1)	0.82(8)	-0.4(1)
C6	2.7(1)	5.0(2)	4.3(1)	0.2(1)	1.0(1)	-0.0(1)
C7	4.0(1)	3.4(1)	3.3(1)	0.2(1)	0.9(1)	-0.4(1)
C8	5.0(1)	4.7(2)	5.3(2)	1.2(1)	2.5(1)	-0.4(1)
C9	4.3(1)	5.2(2)	5.7(1)	1.3(1)	2.8(1)	0.7(1)
C10	2.9(1)	4.6(2)	4.7(1)	0.0(1)	1.4(1)	0.7(1)
C11	2.8(1)	3.4(1)	2.5(1)	0.2(1)	0.62(8)	-0.2(1)
C12	5.3(1)	4.3(2)	3.0(1)	0.7(1)	1.3(1)	0.9(1)
C13	5.6(2)	3.9(1)	3.5(1)	1.3(1)	1.4(1)	0.7(1)
C14	10.6(3)	4.3(2)	5.5(2)	0.5(2)	2.4(2)	1.5(2)
C15	6.4(2)	7.6(2)	6.4(2)	3.1(2)	1.7(1)	0.7(2)
C16	5.9(2)	2.9(1)	3.8(1)	-0.0(1)	1.4(1)	0.1(1)

The form of the anisotropic displacement parameter is:
exp[-0.25{h»a»B(1,1) + k»b»B(2,2) + l»c»B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)}] where a,b, and c are reciprocal lattice constants.

Table of General Displacement Parameter Expressions - U's

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O1	0.068(1)	0.043(1)	0.115(1)	-0.002(1)	0.052(1)	0.024(1)
O2	0.048(1)	0.048(1)	0.074(1)	0.007(1)	0.0296(9)	0.017(1)
O3	0.069(1)	0.059(1)	0.091(2)	-0.016(1)	0.016(1)	-0.032(1)
O4	0.049(1)	0.050(1)	0.0327(9)	0.006(1)	0.0095(8)	0.000(1)
O5	0.059(1)	0.035(1)	0.0345(9)	0.001(1)	0.0151(8)	-0.0014(9)
C1	0.041(1)	0.041(2)	0.047(2)	-0.004(1)	0.014(1)	0.001(1)
C2	0.038(1)	0.045(2)	0.037(1)	0.001(1)	0.007(1)	0.004(1)
C3	0.066(2)	0.071(2)	0.069(2)	0.016(2)	0.031(1)	0.014(2)
C4	0.043(2)	0.037(2)	0.038(1)	-0.001(1)	0.008(1)	-0.001(1)
C5	0.035(1)	0.038(2)	0.036(1)	0.000(1)	0.010(1)	-0.004(1)
C6	0.034(1)	0.064(2)	0.054(2)	0.003(1)	0.013(1)	-0.001(2)
C7	0.051(2)	0.043(2)	0.042(2)	0.002(2)	0.011(1)	-0.005(2)
C8	0.063(2)	0.060(2)	0.067(2)	0.015(2)	0.032(1)	-0.005(2)
C9	0.055(2)	0.065(2)	0.072(2)	0.016(2)	0.036(1)	0.008(2)
C10	0.037(1)	0.059(2)	0.059(2)	0.000(2)	0.018(1)	0.009(2)
C11	0.035(1)	0.043(2)	0.032(1)	0.003(1)	0.008(1)	-0.003(1)
C12	0.067(2)	0.055(2)	0.038(1)	0.009(2)	0.017(1)	0.011(2)
C13	0.071(2)	0.049(2)	0.044(2)	0.017(2)	0.018(1)	0.009(2)
C14	0.134(3)	0.055(2)	0.070(2)	0.006(2)	0.031(2)	0.019(2)
C15	0.081(2)	0.096(3)	0.080(2)	0.040(2)	0.022(2)	0.009(2)
C16	0.075(2)	0.037(2)	0.048(2)	-0.000(2)	0.018(2)	0.001(2)

The form of the anisotropic displacement parameter is:
exp[-2Ð»{h»a»U(1,1) + k»b»U(2,2) + l»c»U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a,b, and c are reciprocal lattice constants.

» means squared (a, b, are a* b*

Table of Refined Displacement Parameter Expressions - Beta's

Name	Ã(1,1)	Ã(2,2)	Ã(3,3)	Ã(1,2)	Ã(1,3)	Ã(2,3)
O1	0.0084(2)	0.0078(2)	0.0161(2)	-0.0005(3)	0.0138(3)	0.0078(4)
O2	0.0060(1)	0.0088(2)	0.0103(2)	0.0020(3)	0.0078(2)	0.0053(4)
O3	0.0086(2)	0.0108(3)	0.0128(2)	-0.0048(4)	0.0044(3)	-0.0103(4)
O4	0.0062(1)	0.0091(2)	0.0046(1)	0.0018(3)	0.0025(2)	0.0001(3)
O5	0.0073(1)	0.0064(2)	0.0048(1)	0.0003(3)	0.0040(2)	-0.0004(3)
C1	0.0051(2)	0.0074(3)	0.0065(2)	-0.0013(4)	0.0038(3)	0.0005(5)
C2	0.0048(2)	0.0082(3)	0.0052(2)	0.0004(4)	0.0019(3)	0.0013(5)
C3	0.0082(2)	0.0130(4)	0.0097(3)	0.0048(6)	0.0082(4)	0.0046(6)
C4	0.0054(2)	0.0067(3)	0.0053(2)	-0.0003(4)	0.0022(3)	-0.0002(4)
C5	0.0044(2)	0.0070(3)	0.0050(2)	0.0001(4)	0.0027(3)	-0.0014(4)
C6	0.0042(2)	0.0116(4)	0.0076(2)	0.0009(5)	0.0035(3)	-0.0002(6)
C7	0.0064(2)	0.0078(3)	0.0059(2)	0.0007(5)	0.0029(3)	-0.0015(5)
C8	0.0079(2)	0.0109(4)	0.0093(3)	0.0045(5)	0.0084(4)	-0.0015(6)
C9	0.0069(2)	0.0119(4)	0.0100(3)	0.0049(5)	0.0095(3)	0.0027(6)
C10	0.0046(2)	0.0107(4)	0.0083(2)	0.0001(5)	0.0048(3)	0.0029(5)
C11	0.0044(2)	0.0077(3)	0.0044(2)	0.0008(4)	0.0021(3)	-0.0009(4)
C12	0.0084(2)	0.0100(4)	0.0054(2)	0.0027(5)	0.0044(3)	0.0036(5)
C13	0.0089(2)	0.0090(3)	0.0062(2)	0.0050(5)	0.0047(4)	0.0028(5)
C14	0.0167(4)	0.0100(4)	0.0098(3)	0.0018(7)	0.0082(5)	0.0059(7)
C15	0.0101(3)	0.0175(5)	0.0113(3)	0.0119(6)	0.0058(5)	0.0027(8)
C16	0.0093(3)	0.0067(3)	0.0068(3)	-0.0000(5)	0.0048(4)	0.0003(5)

The form of the anisotropic displacement parameter is:
exp[-(Ã(1,1)*h» + Ã(2,2)*k» + Ã(3,3)*l» + Ã(1,2)*hk + Ã(1,3)*hl + Ã(2,3)*kl)].

Table of Root-Mean-Square Amplitudes of Anisotropic Displacement in Angstroms

Atom	Min.	Intermediate	Max.
O1	0.161	0.238	0.357
O2	0.190	0.204	0.290
O3	0.190	0.274	0.334
O4	0.181	0.210	0.237
O5	0.179	0.190	0.242
C1	0.187	0.212	0.217
C2	0.185	0.202	0.217
C3	0.222	0.237	0.307
C4	0.190	0.195	0.213
C5	0.177	0.188	0.204
C6	0.180	0.232	0.254
C7	0.194	0.214	0.232
C8	0.185	0.261	0.281
C9	0.181	0.244	0.298
C10	0.183	0.225	0.261
C11	0.176	0.185	0.211
C12	0.180	0.233	0.269
C13	0.193	0.215	0.284
C14	0.205	0.283	0.367
C15	0.219	0.283	0.359
C16	0.192	0.218	0.274

Table of Least-Squares Planes

Orthonormal Equation of Plane 1

-0.2536	X +	0.2535	Y +	-0.9335	Z -	3.7072	= 0
0.0011		0.0009		0.0004		0.0091	

Crystallographic Equation of Plane

-3.3096	X +	2.6393	Y +	-10.2488	Z -	3.7072	= 0
0.0141		0.0098		0.1080		0.0091	

Atom	X	Y	Z	Distance	Esd
C5	5.2119	9.4446	-2.5199	-0.2825	+- 0.0026
C7	5.7216	8.1904	-3.2505	-0.0478	+- 0.0029
C8	7.2038	8.0431	-3.4855	-0.2416	+- 0.0033
C9	7.9383	9.3110	-3.8617	0.2446	+- 0.0032
C10	7.5223	10.4750	-2.9636	-0.1932	+- 0.0031
C11	6.0008	10.6759	-3.0332	0.3087	+- 0.0026
O3	4.9545	7.3152	-3.5578	0.2118	+- 0.0024

Chi Squared = 49141.7

Orthonormal Equation of Plane 2

-0.9999	X +	-0.0047	Y +	0.0128	Z -	-5.9001	= 0
0.0001		0.0013		0.0050		0.0236	

Crystallographic Equation of Plane

-13.0479	X +	-0.0488	Y +	3.4345	Z -	-5.9001	= 0
0.0008		0.0140		0.0655		0.0236	

Atom	X	Y	Z	Distance	Esd
C11	6.0008	10.6759	-3.0332	-0.1890	+- 0.0027
O4	5.5897	10.8292	-4.3835	0.2042	+- 0.0019
C12	6.0358	12.0394	-5.0034	-0.2556	+- 0.0035
C13	5.5745	13.2634	-4.2113	0.2102	+- 0.0035
C16	6.0091	13.0608	-2.7786	-0.2052	+- 0.0035
O5	5.5811	11.7863	-2.2547	0.2354	+- 0.0019

Chi Squared = 43080.9

Dihedral Angles Between Planes:

Plane No.	Plane No.	Dihedral Angle

1	2	76.08 +- 0.29

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
H25	O1	C1	O2	85.30 (10.39)
H25	O1	C1	C2	-92.11 (10.37)
C12	O4	C11	O5	55.99 (0.29)
C12	O4	C11	C5	170.69 (0.22)
C12	O4	C11	C10	-67.97 (0.30)
C11	O4	C12	C13	-56.70 (0.32)
C11	O4	C12	H9	-177.22 (0.25)
C11	O4	C12	H10	65.55 (0.32)
C16	O5	C11	O4	-54.54 (0.29)
C16	O5	C11	C5	-167.88 (0.22)
C16	O5	C11	C10	68.50 (0.29)
C11	O5	C16	C13	55.27 (0.33)
C11	O5	C16	H17	-67.85 (0.32)
C11	O5	C16	H18	176.94 (0.25)
O1	C1	C2	C3	9.92 (0.41)
O1	C1	C2	C4	-174.88 (0.25)
O1	C1	C2	H24	-74.06 (0.34)
O2	C1	C2	C3	-167.52 (0.29)
O2	C1	C2	C4	7.68 (0.40)
O2	C1	C2	H24	108.50 (0.32)
C1	C2	C3	H1	-58.59 (0.42)
C1	C2	C3	H2	63.11 (0.41)
C1	C2	C3	H26	-179.31 (0.27)
C4	C2	C3	H1	126.48 (0.33)
C4	C2	C3	H2	-111.83 (0.35)
C4	C2	C3	H26	5.75 (0.46)
H24	C2	C3	H1	47.70 (0.32)
H24	C2	C3	H2	169.40 (0.35)
H24	C2	C3	H26	-73.03 (0.31)
C1	C2	C4	C5	91.16 (0.31)
C1	C2	C4	H22	-30.03 (0.35)
C1	C2	C4	H23	-146.74 (0.26)
C3	C2	C4	C5	-93.89 (0.35)
C3	C2	C4	H22	144.91 (0.30)
C3	C2	C4	H23	28.20 (0.41)
H24	C2	C4	C5	-22.45 (0.30)
H24	C2	C4	H22	-143.65 (0.25)
H24	C2	C4	H23	99.64 (0.27)
C2	C4	C5	C6	59.65 (0.32)
C2	C4	C5	C7	-59.93 (0.31)
C2	C4	C5	C11	-178.88 (0.23)
H22	C4	C5	C6	-179.05 (0.25)
H22	C4	C5	C7	61.37 (0.31)
H22	C4	C5	C11	-57.58 (0.31)
H23	C4	C5	C6	-62.61 (0.32)
H23	C4	C5	C7	177.81 (0.24)
H23	C4	C5	C11	58.87 (0.31)
C4	C5	C6	H19	61.47 (0.33)
C4	C5	C6	H20	-179.21 (0.27)
C4	C5	C6	H21	-57.86 (0.33)
C7	C5	C6	H19	-179.26 (0.25)
C7	C5	C6	H20	-59.94 (0.35)
C7	C5	C6	H21	61.41 (0.32)

Table of Torsion Angles in Degrees (continued)

Atom 1	Atom 2	Atom 3	Atom 4	Angle	
C11	C5	C6	H19	-59.25	(0.32)
C11	C5	C6	H20	60.07	(0.35)
C11	C5	C6	H21	-178.58	(0.24)
C4	C5	C7	O3	97.30	(0.31)
C4	C5	C7	C8	-78.61	(0.31)
C6	C5	C7	O3	-22.00	(0.37)
C6	C5	C7	C8	162.10	(0.26)
C11	C5	C7	O3	-143.25	(0.27)
C11	C5	C7	C8	40.84	(0.33)
C4	C5	C11	O4	-173.30	(0.21)
C4	C5	C11	O5	-56.00	(0.27)
C4	C5	C11	C10	67.04	(0.29)
C6	C5	C11	O4	-52.87	(0.27)
C6	C5	C11	O5	64.43	(0.27)
C6	C5	C11	C10	-172.53	(0.23)
C7	C5	C11	O4	67.59	(0.26)
C7	C5	C11	O5	-175.11	(0.21)
C7	C5	C11	C10	-52.06	(0.29)
O3	C7	C8	C9	144.90	(0.30)
O3	C7	C8	H3	22.69	(0.43)
O3	C7	C8	H4	-93.54	(0.37)
C5	C7	C8	C9	-39.22	(0.38)
C5	C7	C8	H3	-161.43	(0.26)
C5	C7	C8	H4	82.33	(0.36)
C7	C8	C9	C10	45.41	(0.36)
C7	C8	C9	H5	-74.91	(0.36)
C7	C8	C9	H6	169.70	(0.27)
H3	C8	C9	C10	166.97	(0.28)
H3	C8	C9	H5	46.65	(0.40)
H3	C8	C9	H6	-68.73	(0.39)
H4	C8	C9	C10	-77.24	(0.35)
H4	C8	C9	H5	162.44	(0.30)
H4	C8	C9	H6	47.06	(0.40)
C8	C9	C10	C11	-56.53	(0.33)
C8	C9	C10	H7	66.75	(0.35)
C8	C9	C10	H8	-176.19	(0.27)
H5	C9	C10	C11	63.16	(0.35)
H5	C9	C10	H7	-173.55	(0.28)
H5	C9	C10	H8	-56.50	(0.37)
H6	C9	C10	C11	179.65	(0.27)
H6	C9	C10	H7	-57.06	(0.39)
H6	C9	C10	H8	59.99	(0.38)
C9	C10	C11	O4	-54.22	(0.31)
C9	C10	C11	O5	-177.52	(0.23)
C9	C10	C11	C5	62.23	(0.30)
H7	C10	C11	O4	-176.99	(0.25)
H7	C10	C11	O5	59.71	(0.34)
H7	C10	C11	C5	-60.54	(0.34)
H8	C10	C11	O4	66.21	(0.32)
H8	C10	C11	O5	-57.09	(0.32)
H8	C10	C11	C5	-177.35	(0.24)
O4	C12	C13	C14	170.21	(0.27)

O4	C12	C13	C15	-68.00 (0.33)
O4	C12	C13	C16	52.64 (0.34)

Table of Torsion Angles in Degrees (continued)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
H9	C12	C13	C14	-69.34 (0.38)
H9	C12	C13	C15	52.44 (0.38)
H9	C12	C13	C16	173.08 (0.29)
H10	C12	C13	C14	48.25 (0.38)
H10	C12	C13	C15	170.04 (0.29)
H10	C12	C13	C16	-69.32 (0.35)
C12	C13	C14	H11	61.62 (0.47)
C12	C13	C14	H12	-175.23 (0.34)
C12	C13	C14	H13	-58.27 (0.40)
C15	C13	C14	H11	-60.13 (0.47)
C15	C13	C14	H12	63.01 (0.45)
C15	C13	C14	H13	179.98 (0.33)
C16	C13	C14	H11	178.34 (0.36)
C16	C13	C14	H12	-58.51 (0.46)
C16	C13	C14	H13	58.44 (0.40)
C12	C13	C15	H14	-60.46 (0.42)
C12	C13	C15	H15	57.84 (0.42)
C12	C13	C15	H16	179.52 (0.32)
C14	C13	C15	H14	60.55 (0.43)
C14	C13	C15	H15	178.85 (0.32)
C14	C13	C15	H16	-59.47 (0.43)
C16	C13	C15	H14	-179.10 (0.32)
C16	C13	C15	H15	-60.79 (0.42)
C16	C13	C15	H16	60.89 (0.43)
C12	C13	C16	O5	-52.23 (0.35)
C12	C13	C16	H17	69.72 (0.35)
C12	C13	C16	H18	-173.27 (0.29)
C14	C13	C16	O5	-170.19 (0.28)
C14	C13	C16	H17	-48.24 (0.39)
C14	C13	C16	H18	68.78 (0.39)
C15	C13	C16	O5	68.33 (0.35)
C15	C13	C16	H17	-169.72 (0.29)
C15	C13	C16	H18	-52.70 (0.39)

PERFACT (1.4.9) 12/12/96 15:17:15
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STATISTICS BASED ON DATA COLLECTION ORDER.

Minimum	Maximum	No.contrib.	Av Fo	Av ô °Fo-Fc°»	R	Rw	Error
1	100	81	39.	12.433	0.050	0.081	3.741
101	200	85	26.	11.677	0.055	0.083	3.626
201	300	87	18.	10.247	0.063	0.083	3.396
301	400	79	19.	9.031	0.060	0.079	3.189
401	500	77	16.	6.995	0.054	0.072	2.806
501	600	76	12.	7.017	0.060	0.078	2.810
601	700	70	11.	3.388	0.047	0.059	1.953
701	800	77	12.	3.182	0.042	0.056	1.893
801	900	63	12.	2.243	0.038	0.048	1.589
901	1000	73	12.	2.550	0.037	0.049	1.694
1001	1100	72	11.	3.292	0.049	0.061	1.925
1101	1200	67	11.	3.488	0.050	0.063	1.982
1201	1300	63	11.	2.637	0.043	0.054	1.723
1301	1400	70	11.	2.863	0.049	0.057	1.795
1401	1500	69	10.	4.252	0.061	0.077	2.188
1501	1600	62	10.	2.832	0.055	0.061	1.786
1601	1700	59	8.	1.875	0.055	0.058	1.453
1701	1800	52	9.	2.165	0.051	0.057	1.561
1801	1900	52	7.	1.858	0.063	0.067	1.446
1901	2000	52	7.	1.203	0.053	0.057	1.164
2001	2100	33	9.	2.249	0.056	0.062	1.591
2101	2200	34	7.	2.612	0.082	0.086	1.715
2201	2300	45	7.	2.650	0.092	0.091	1.727
2301	2400	42	7.	2.298	0.086	0.091	1.608
2401	2500	33	7.	2.676	0.088	0.095	1.736
2501	2600	26	7.	2.862	0.106	0.108	1.795
2601	2700	30	7.	2.348	0.076	0.091	1.626
2701	2800	23	6.	1.039	0.072	0.073	1.082
2801	2900	25	6.	3.752	0.123	0.137	2.055
2901	3000	23	7.	2.421	0.095	0.112	1.651
3001	3100	1	5.	2.426	0.213	0.213	1.653

PERFACT (1.4.9) 12/12/96 15:17:15
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STATISTICS BASED ON MAGNITUDE OF F(OBS).

Minimum	Maximum	No.contrib.	Av Fo	Av ð °Fo-Fc°»	R	Rw	Error
		86	57.	6.412	0.046	0.053	2.687
		86	30.	5.033	0.038	0.050	2.380
		86	22.	4.003	0.035	0.048	2.123
		86	18.	4.457	0.035	0.052	2.240
		86	16.	3.277	0.034	0.045	1.921
		86	14.	7.482	0.050	0.069	2.902
		86	12.	4.954	0.047	0.060	2.361
		86	11.	4.844	0.046	0.063	2.335
		86	10.	4.400	0.053	0.067	2.226
		86	9.	3.964	0.051	0.068	2.112
		86	8.	5.970	0.060	0.093	2.592
		86	7.	4.573	0.072	0.092	2.269
		86	7.	4.046	0.075	0.094	2.134
		86	6.	5.297	0.089	0.129	2.442
		86	6.	3.790	0.085	0.116	2.066
		86	5.	6.017	0.111	0.165	2.603
		86	5.	3.753	0.133	0.169	2.056
		86	4.	2.329	0.124	0.143	1.619
		86	4.	3.622	0.165	0.205	2.019
		67	3.	5.598	0.242	0.273	2.510

Maximum Fo = 225.42
Scale factor = 0.2503

PERFACT (1.4.9) 12/12/96 15:17:15
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STATISTICS BASED ON SIN(THETA)/LAMBDA.

Minimum	Maximum	No.contrib.	Av Fo	Av ð °Fo-Fc°»	R	Rw	Error
0.05	0.10	14	65.	14.596	0.067	0.084	4.054
0.10	0.15	24	34.	25.321	0.053	0.123	5.339
0.15	0.20	66	31.	6.295	0.040	0.058	2.662
0.20	0.25	96	23.	12.666	0.063	0.088	3.776
0.25	0.30	140	18.	8.425	0.057	0.076	3.080
0.30	0.35	171	13.	6.616	0.056	0.074	2.729
0.35	0.40	214	11.	2.940	0.041	0.054	1.819
0.40	0.45	269	11.	2.912	0.045	0.056	1.811
0.45	0.50	296	9.	2.928	0.055	0.064	1.816
0.50	0.55	250	7.	2.079	0.071	0.074	1.530
0.55	0.60	161	7.	2.540	0.093	0.103	1.691

Maximum sin(Õ)/lambda = 0.5941

PERFACT (1.4.9) 12/12/96 15:17:16
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STATISTICS BASED ON INDICES -- VALUE OF H.

Minimum	Maximum	No.contrib.	Av Fo	Av σ °Fo-Fc°»	R	Rw	Error
0	0	91	20.	6.355	0.046	0.073	2.675
1	1	180	16.	4.511	0.043	0.063	2.253
2	2	178	19.	6.342	0.059	0.073	2.672
3	3	154	14.	6.941	0.056	0.079	2.795
4	4	181	12.	5.122	0.057	0.074	2.401
5	5	144	11.	5.781	0.067	0.080	2.551
6	6	145	13.	5.204	0.059	0.074	2.420
7	7	136	10.	2.987	0.053	0.061	1.834
8	8	129	11.	3.577	0.057	0.067	2.007
9	9	104	10.	2.748	0.050	0.059	1.759
10	10	93	10.	2.600	0.053	0.059	1.711
11	11	66	8.	2.937	0.071	0.077	1.818
12	12	50	8.	3.270	0.064	0.081	1.919
13	13	25	7.	2.143	0.078	0.090	1.553
14	14	22	6.	2.358	0.094	0.096	1.629
15	15	3	6.	0.686	0.067	0.063	0.879

PERFACT (1.4.9) 12/12/96 15:17:16
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STATISTICS BASED ON INDICES -- VALUE OF K.

Minimum	Maximum	No.contrib.	Av Fo	Av ð °Fo-Fc°»	R	Rw	Error
0	0	123	21.	7.640	0.058	0.079	2.933
1	1	221	17.	5.868	0.050	0.072	2.570
2	2	228	12.	4.936	0.055	0.073	2.357
3	3	213	13.	4.998	0.055	0.069	2.372
4	4	204	14.	5.889	0.053	0.075	2.575
5	5	173	13.	4.466	0.056	0.066	2.242
6	6	163	9.	3.113	0.054	0.064	1.872
7	7	126	8.	3.167	0.064	0.074	1.888
8	8	100	10.	3.305	0.062	0.070	1.929
9	9	79	10.	1.652	0.048	0.049	1.364
10	10	44	7.	2.664	0.079	0.080	1.732
11	11	17	6.	3.124	0.112	0.136	1.875
12	12	10	6.	2.397	0.114	0.121	1.643

pERFACT (1.4.9) 12/12/96 15:17:16
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STATISTICS BASED ON INDICES -- VALUE OF L.

Minimum	Maximum	No.contrib.	Av Fo	Av ô °Fo-Fc°»	R	Rw	Error
-14	-14	10	7.	0.805	0.043	0.059	0.952
-13	-13	14	9.	3.429	0.078	0.080	1.965
-12	-12	34	8.	1.599	0.056	0.056	1.342
-11	-11	41	8.	2.661	0.062	0.068	1.731
-10	-10	50	9.	2.406	0.056	0.064	1.646
-9	-9	50	11.	2.221	0.041	0.050	1.581
-8	-8	66	10.	3.696	0.056	0.067	2.040
-7	-7	72	10.	4.853	0.066	0.081	2.337
-6	-6	94	11.	5.543	0.065	0.080	2.498
-5	-5	96	12.	5.586	0.065	0.078	2.508
-4	-4	96	13.	4.390	0.052	0.066	2.223
-3	-3	99	15.	5.837	0.060	0.073	2.563
-2	-2	98	16.	8.005	0.064	0.084	3.002
-1	-1	96	18.	9.977	0.071	0.094	3.351
0	0	92	15.	6.821	0.055	0.082	2.771
1	1	95	16.	5.029	0.045	0.067	2.379
2	2	99	14.	4.923	0.049	0.069	2.354
3	3	83	15.	3.874	0.047	0.061	2.088
4	4	82	15.	2.911	0.039	0.051	1.810
5	5	78	13.	2.741	0.044	0.054	1.757
6	6	71	11.	2.513	0.048	0.056	1.682
7	7	60	11.	3.586	0.054	0.065	2.009
8	8	48	11.	3.010	0.047	0.062	1.841
9	9	31	10.	2.143	0.055	0.057	1.553
10	10	18	8.	3.275	0.074	0.079	1.920
11	11	17	6.	3.480	0.108	0.115	1.979
12	12	6	7.	2.615	0.083	0.097	1.716
13	13	5	6.	2.852	0.128	0.130	1.792

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STATISTICS BASED ON CLASSES OF INDICES.

Class	No.contrib.	Av Fo	Av ô °Fo-Fc°»	R	Rw	Error
eee	252	13.	5.556	0.054	0.078	2.501
eeo	228	15.	5.042	0.058	0.071	2.383
eoe	200	13.	4.246	0.055	0.069	2.186
eoo	209	13.	4.347	0.058	0.069	2.212
oee	208	11.	3.867	0.054	0.068	2.086
oeo	184	11.	4.845	0.060	0.076	2.335
ooe	204	13.	4.172	0.052	0.065	2.167
ooo	216	12.	5.129	0.052	0.073	2.403
h odd	812	12.	4.501	0.054	0.070	2.251
h even	889	14.	4.845	0.056	0.072	2.336
k odd	829	13.	4.483	0.054	0.069	2.247
k even	872	13.	4.869	0.056	0.073	2.341
l odd	837	13.	4.848	0.057	0.072	2.336
l even	864	13.	4.519	0.054	0.071	2.256
h+k odd	801	12.	4.311	0.057	0.070	2.203
h+k even	900	14.	5.010	0.054	0.072	2.375
h+l odd	849	13.	4.374	0.056	0.068	2.219
h+l even	852	12.	4.987	0.055	0.074	2.369
k+l odd	816	13.	4.585	0.056	0.070	2.272
k+l even	885	12.	4.769	0.055	0.072	2.317
h+k+l odd	852	13.	4.590	0.055	0.070	2.273
h+k+l even	849	13.	4.772	0.055	0.072	2.318
all data	1701	13.	4.681	0.055	0.071	2.296

PERFACT (1.4.9) 12/12/96 15:17:16
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STATISTICS BASED ON WEIGHTING SCHEME. ERROR VS. FOBS.

Av Fo	p=0.00	p=0.01	p=0.02	p=0.03	p=0.04	p=0.05	p=0.06	p=0.07	p=0.08
57.	12.668	7.852	4.911	3.490	2.687	2.178	1.829	1.575	1.382
30.	6.070	5.170	3.887	2.982	2.383	1.970	1.674	1.453	1.282
22.	4.092	3.767	3.139	2.567	2.127	1.798	1.549	1.356	1.204
18.	4.011	3.759	3.220	2.682	2.245	1.908	1.649	1.447	1.286
16.	3.277	3.097	2.696	2.278	1.925	1.647	1.430	1.258	1.121
14.	5.024	4.734	4.100	3.450	2.909	2.485	2.155	1.895	1.687
12.	3.742	3.573	3.183	2.752	2.370	2.055	1.802	1.597	1.430
11.	3.459	3.333	3.029	2.676	2.346	2.064	1.830	1.636	1.474
10.	3.126	3.028	2.791	2.510	2.240	2.002	1.797	1.623	1.475
9.	2.867	2.787	2.592	2.358	2.129	1.923	1.742	1.585	1.450
8.	3.588	3.481	3.219	2.909	2.613	2.352	2.128	1.937	1.773
7.	2.766	2.722	2.608	2.459	2.300	2.144	1.997	1.862	1.738
7.	2.579	2.542	2.443	2.310	2.166	2.024	1.890	1.767	1.655
6.	2.995	2.944	2.815	2.650	2.481	2.322	2.175	2.041	1.920
6.	2.405	2.380	2.312	2.215	2.105	1.993	1.884	1.781	1.686
5.	3.099	3.059	2.953	2.809	2.653	2.499	2.355	2.223	2.103
5.	2.228	2.221	2.201	2.168	2.126	2.077	2.023	1.966	1.908
4.	1.751	1.747	1.735	1.715	1.690	1.661	1.629	1.596	1.561
4.	2.171	2.168	2.157	2.141	2.118	2.091	2.060	2.025	1.988
3.	2.698	2.695	2.685	2.668	2.647	2.620	2.589	2.554	2.516
Av error	3.731	3.353	2.934	2.589	2.313	2.091	1.909	1.759	1.632
Av diff.	1.322	0.887	0.524	0.318	0.227	0.197	0.221	0.246	0.265

TEST FOR EXTINCTION.

A plot of intensity(calc) / intensity(obs) versus intensity(calc)
will have an intercept of 1.0 And a slope of 2G.
From a least-squares line thru this plot the following were obtained:
Intercept = 0.999 Slope = -3.3511E-08

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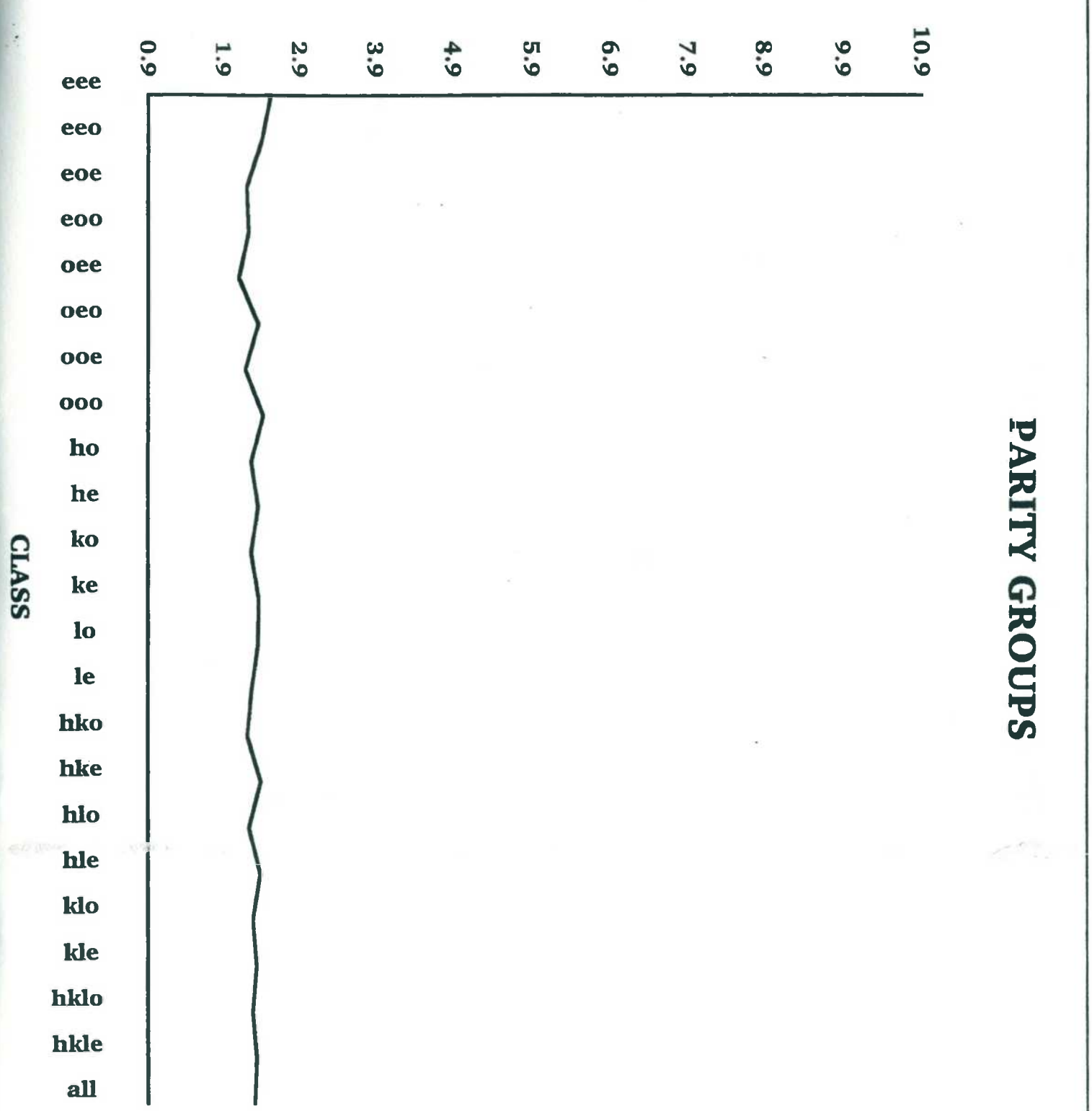
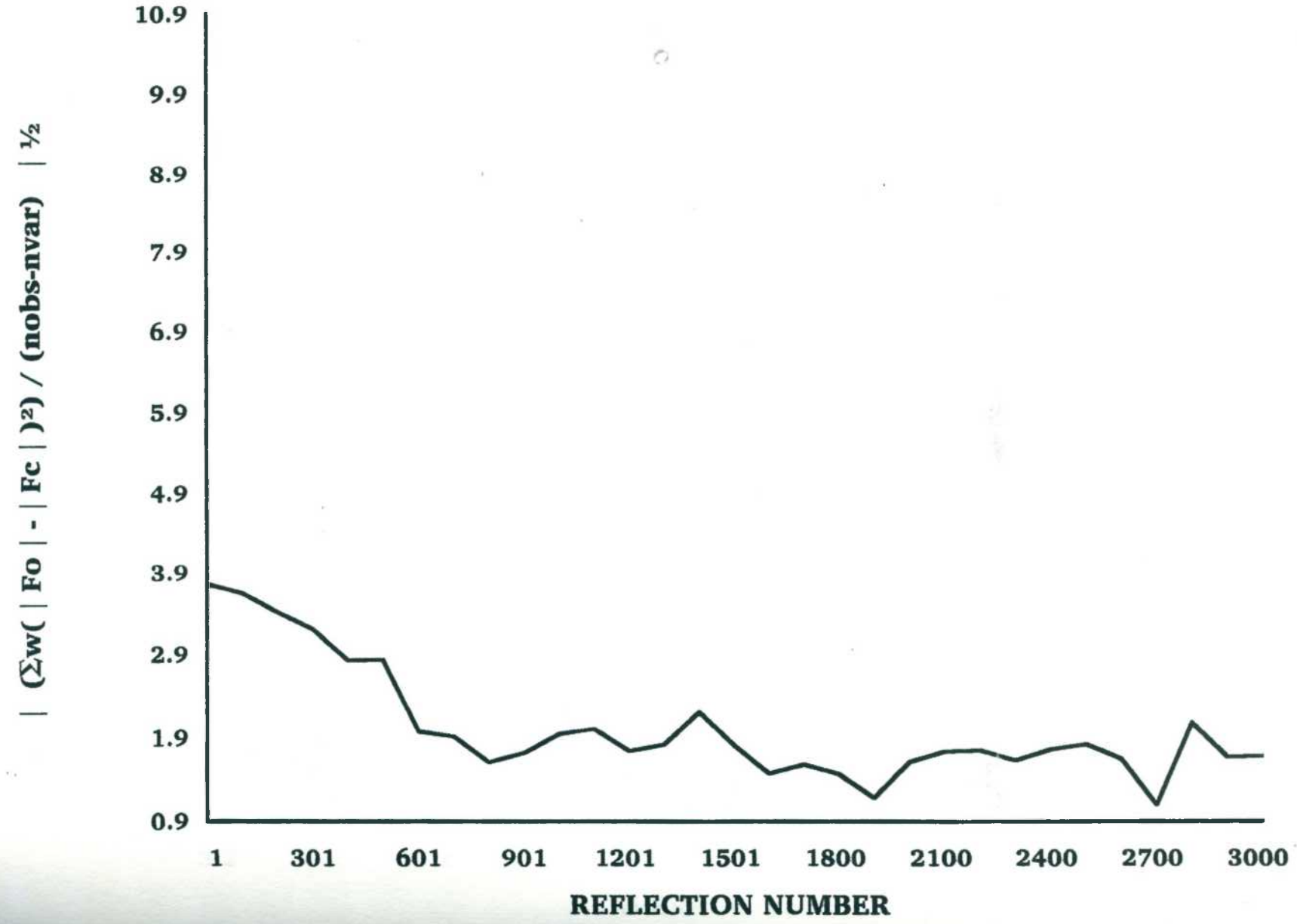
ABLE OF 40 WORST REFLECTIONS.

EL = °Fo-Fc°

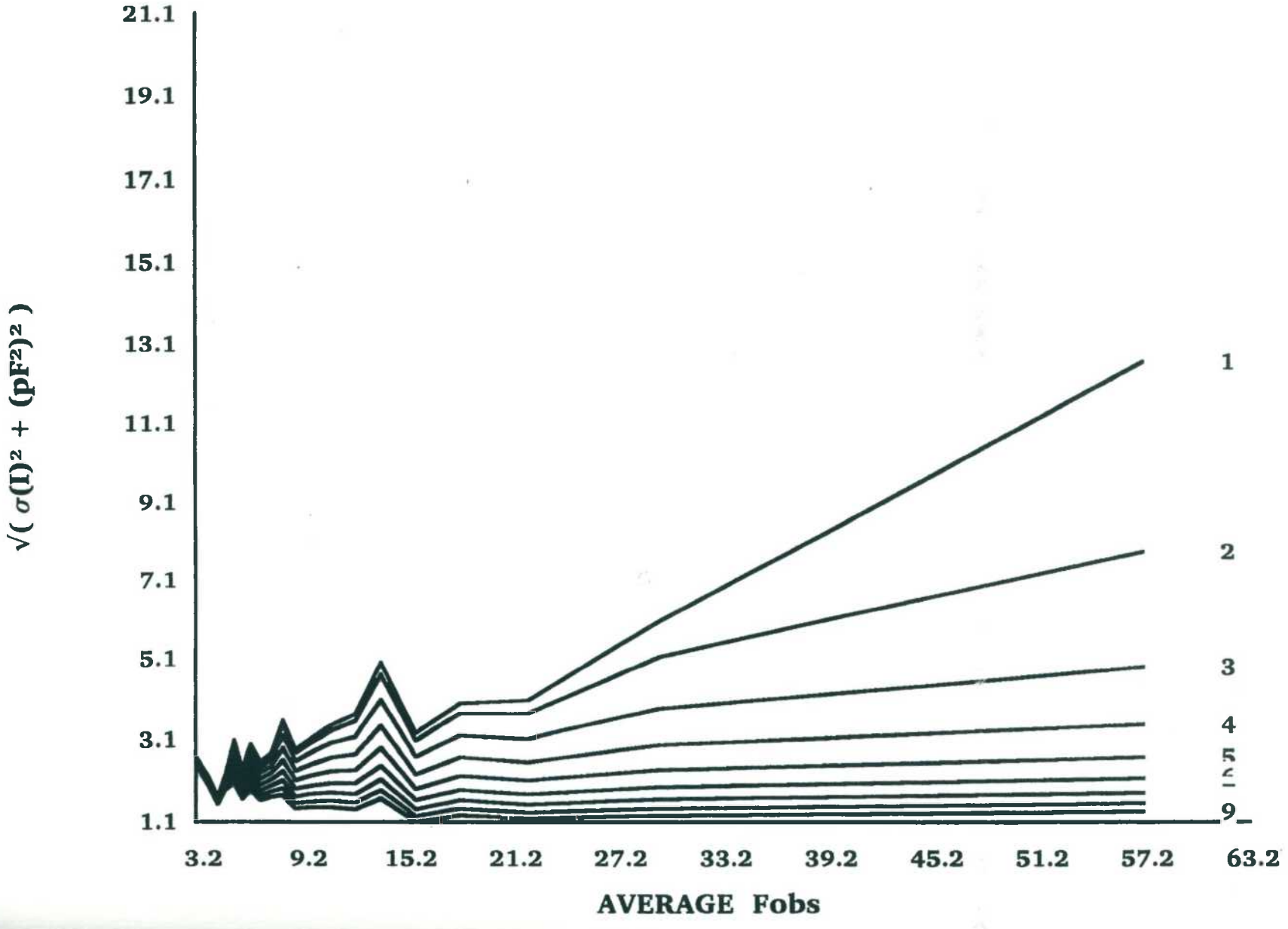
No.	h	k	l	Fo	Fc	sinÕ/l	Phase	Weight	DEL	Í(F)	DEL/Í	DEL/Fo	W*DEL»
31	3	1	-1	5.5	7.4	0.1250	180.	35.84	-1.95	0.125	15.7	0.356	136.92
142	2	4	-1	7.9	10.3	0.2079	180.	23.30	-2.38	0.132	18.0	0.301	132.06
191	6	0	-2	19.3	14.2	0.2308	180.	4.73	5.11	0.249	20.5	0.265	123.48
35	0	2	2	6.2	8.1	0.1278	180.	34.01	-1.86	0.117	15.9	0.300	117.78
111	0	4	0	5.2	7.0	0.1921	0.	28.98	-1.75	0.151	11.6	0.333	88.52
274	4	0	-6	8.3	10.4	0.2602	0.	20.19	-2.04	0.146	14.0	0.245	84.41
237	4	4	-2	13.4	10.4	0.2493	180.	9.06	2.94	0.196	15.0	0.220	78.24
19	1	2	0	13.2	16.0	0.1040	0.	9.84	-2.77	0.177	15.6	0.209	75.34
26	1	2	1	13.2	16.0	0.1161	0.	9.52	-2.76	0.185	14.9	0.208	72.55
11	2	1	0	13.2	15.7	0.0929	180.	10.29	-2.52	0.164	15.4	0.190	65.22
180	4	3	-3	7.4	5.7	0.2265	0.	24.46	1.63	0.137	11.9	0.222	65.12
165	3	1	-5	5.9	7.5	0.2179	0.	26.27	-1.56	0.153	10.2	0.263	64.27
345	2	0	-7	4.8	6.8	0.2842	180.	15.19	-1.99	0.232	8.6	0.414	60.41
353	3	4	-5	28.0	23.2	0.2865	0.	2.58	4.81	0.272	17.7	0.172	59.77
1435	12	0	-2	10.5	8.2	0.4618	0.	9.88	2.30	0.236	9.7	0.219	52.10
511	2	0	7	20.9	17.2	0.3252	0.	3.71	3.74	0.305	12.3	0.178	51.79
508	8	2	-1	6.3	4.5	0.3240	180.	15.71	1.80	0.215	8.4	0.285	50.65
416	6	4	-1	6.5	8.2	0.3004	0.	17.66	-1.67	0.196	8.5	0.256	49.27
269	5	3	1	7.1	5.6	0.2579	180.	21.40	1.51	0.161	9.3	0.213	48.71
40	3	1	-2	8.6	10.2	0.1352	180.	18.97	-1.60	0.152	10.5	0.187	48.35
572	0	0	8	7.5	9.4	0.3370	0.	13.88	-1.82	0.219	8.3	0.241	45.89
1071	5	7	-5	7.9	5.8	0.4178	0.	10.33	2.07	0.264	7.8	0.262	44.08
16	2	0	-2	38.2	43.1	0.0992	180.	1.65	-4.88	0.152	32.0	0.128	39.24
1458	12	1	-2	8.7	10.8	0.4643	0.	9.32	-2.04	0.273	7.5	0.233	38.71
21	1	2	-1	2.4	3.8	0.1081	0.	19.46	-1.41	0.212	6.6	0.579	38.70
443	6	3	2	4.0	5.9	0.3090	180.	9.61	-1.95	0.301	6.5	0.491	36.61
313	2	5	-3	10.3	8.6	0.2731	0.	13.22	1.65	0.181	9.2	0.161	36.34
204	6	1	-2	32.4	28.3	0.2358	0.	2.08	4.15	0.244	17.0	0.128	35.85
539	1	6	-4	8.2	6.8	0.3308	0.	15.66	1.46	0.189	7.7	0.177	33.27
681	1	7	-3	10.4	8.8	0.3576	0.	12.70	1.62	0.187	8.7	0.156	33.22
203	3	4	1	5.2	4.0	0.2357	180.	23.67	1.18	0.174	6.8	0.226	33.06
499	5	5	1	11.7	13.3	0.3216	180.	11.09	-1.68	0.188	9.0	0.144	31.41
210	5	3	-1	17.2	15.0	0.2400	180.	6.06	2.25	0.214	10.5	0.131	30.81
6	2	0	-1	225.4	200.6	0.0794	0.	0.05	24.78	0.467	53.0	0.110	29.88
174	3	4	-1	3.7	2.5	0.2241	180.	18.52	1.26	0.214	5.9	0.337	29.39
369	1	5	-4	13.8	12.0	0.2899	180.	8.63	1.82	0.199	9.2	0.132	28.52
270	4	4	-3	55.6	49.5	0.2597	180.	0.77	6.09	0.253	24.0	0.109	28.44
450	3	6	-1	11.6	13.1	0.3104	180.	11.47	-1.57	0.182	8.6	0.135	28.10
359	3	3	-6	9.4	10.7	0.2877	0.	15.90	-1.32	0.165	8.0	0.141	27.67
255	3	1	-6	8.5	7.3	0.2536	180.	19.92	1.17	0.145	8.0	0.138	27.21


| (Σw(| Fo | - | Fc |)²) / (nobs-nvar) | ½
0.9
1.9
2.9
3.9
4.9
5.9
6.9
7.9
8.9
9.9
10.9
eee
eeo
eoe
eoo
oee
oeo
ooe
ooo
ho
he
ko
ke
lo
le
hko
hke
hlo
hle
klo
kle
hklo
hkle
all
CLASS
PARITY GROUPS

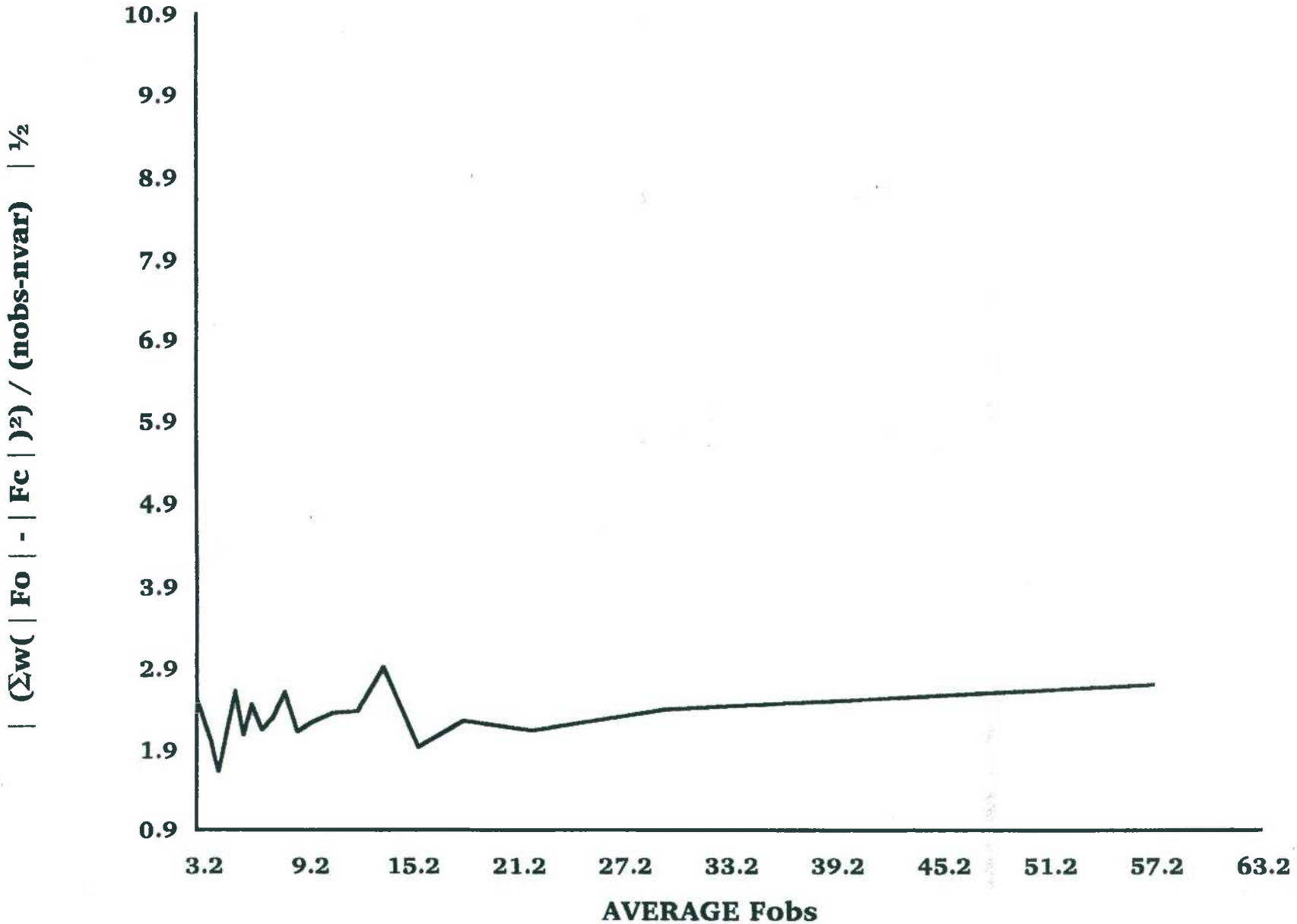
DATA COLLECTION ORDER



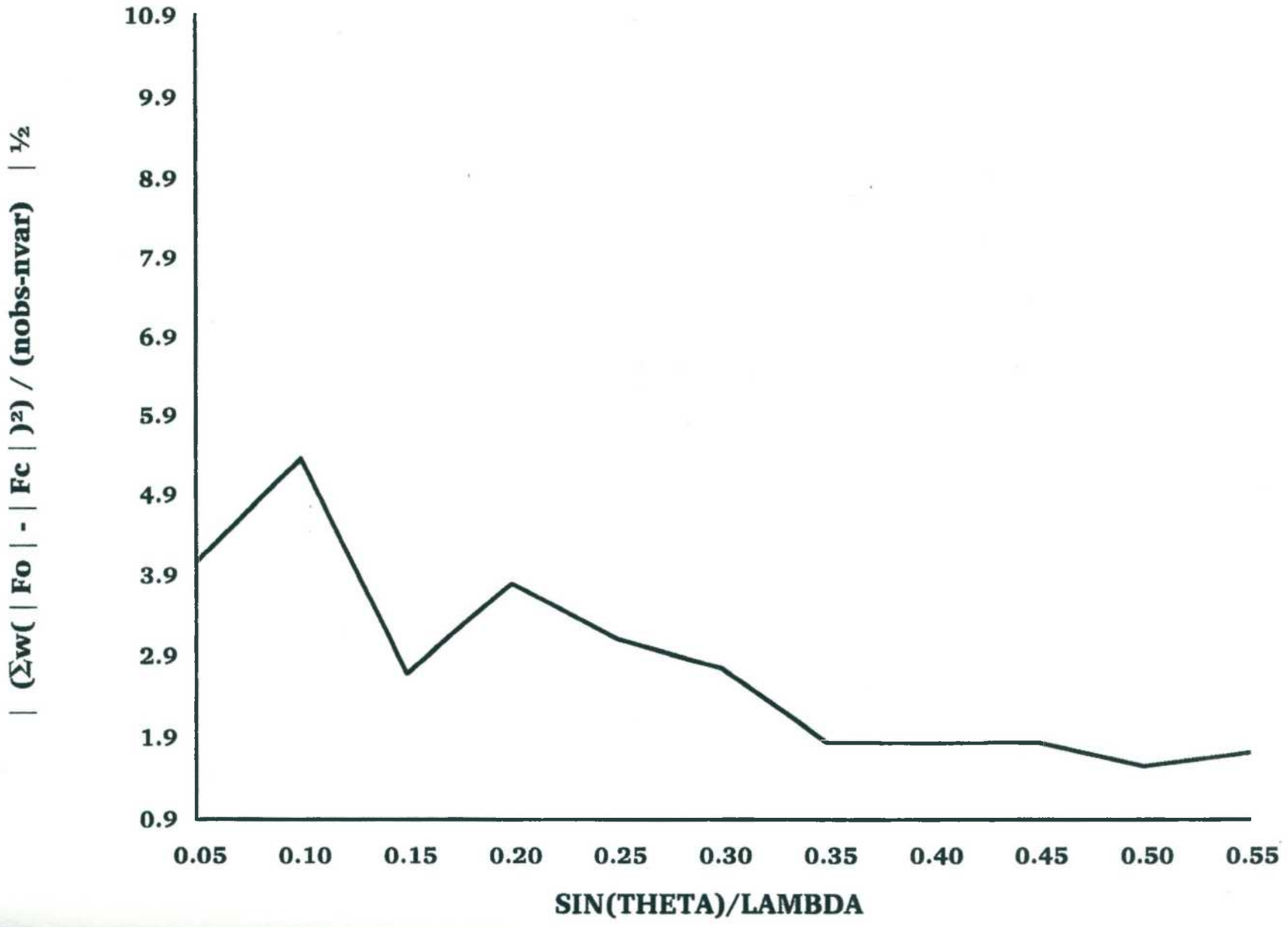
WEIGHTING SCHEME ANALYSIS



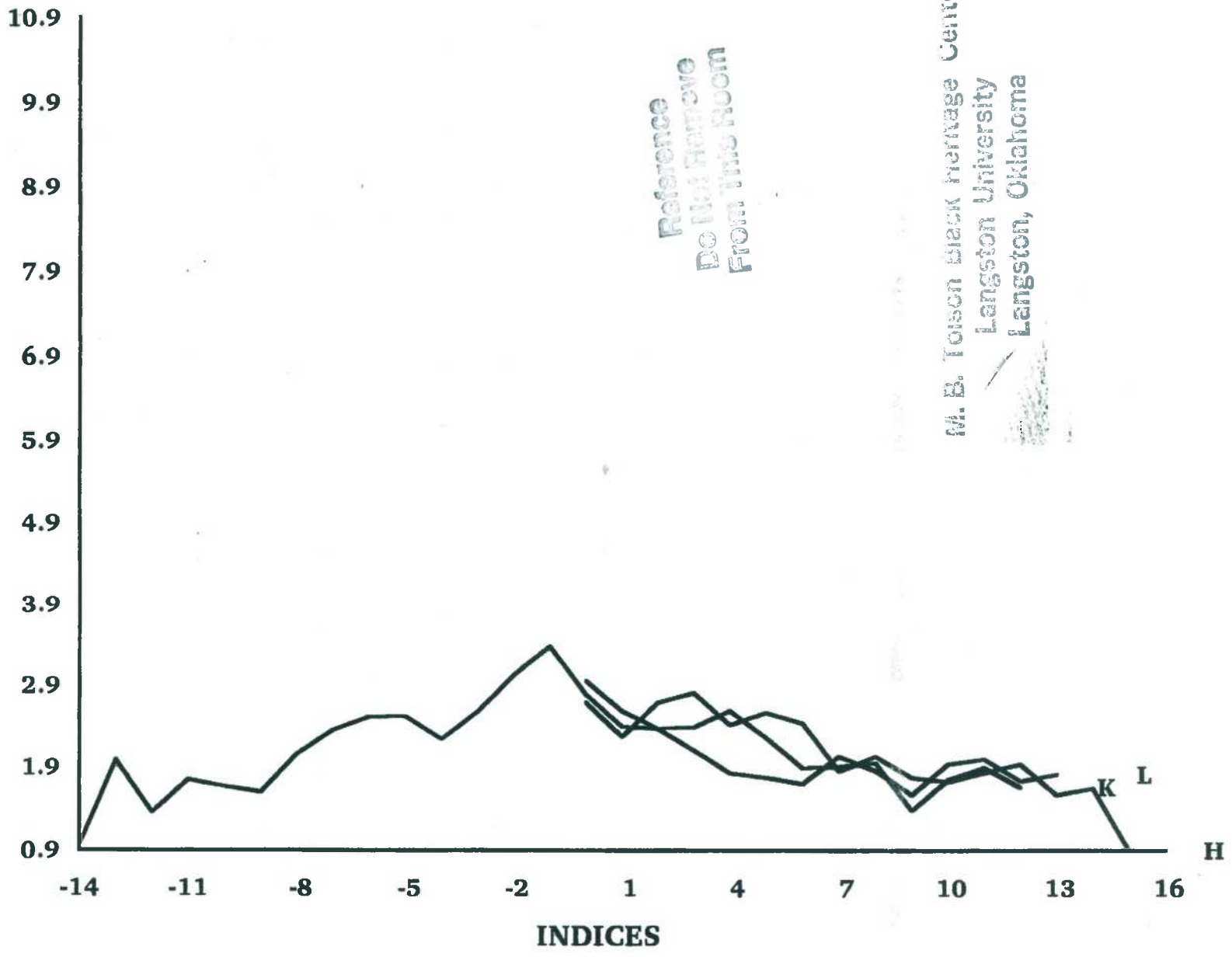
MAGNITUDE OF Fobs



SIN(THETA)/LAMBDA



STATISTICS BASED ON INDICES



CHAPTER V

DISCUSSION

The cyclohexanone ring adopts a chair conformation with the methyl and acrylyl groups in axial and equatorial positions respectively. The dihedral angle between the two mean planes is 73°, which is nearly perpendicular, and a least-square plane calculation indicates that the rings are not individually planar. Following the Cremer and Pople notation (1975), the ring puckering parameters for the cylohexanone ring are $Q_2 = 0.1553$ Å and $\varnothing_2 = +78.1$ Å. The angles around C(10), the spiro carbon, are 110.5°, 106.6°, 111.4°, 104.8°,110.3°and 113.0° which are all nearly tetrahedral. Two of the three of the largest angles around C(10) are endocylic. O(4)-C(10)-O(5) and O(5)-C(10)-C(9) have values of 110.5° and 110.3 ° respectively. These exceed the normal sp^3 values due to the strain of bonding to the oxygens within the compression of the ring system. The largest angle is on C(9) due to the strain of the methyl and acrylyl groups bonded at the C(5) atom. The two oxygens are in the axial position (with respect to the opposite ring). The atoms C(15) and C(16) are respectively equatorial and axial. The acryly group {O(1)-C(1)-C(2) has its delocalization more distributed over the three bonds. Therefore, the bond distance between O(2) and C(1) {1.224 Å) is closer to those observed in aldehydes, ketones and α-oxalic acid. The C(1)-C(2) bond correlates to those observed in analog derivatives. The diagram of the molecule on the following page illustrates the structure.

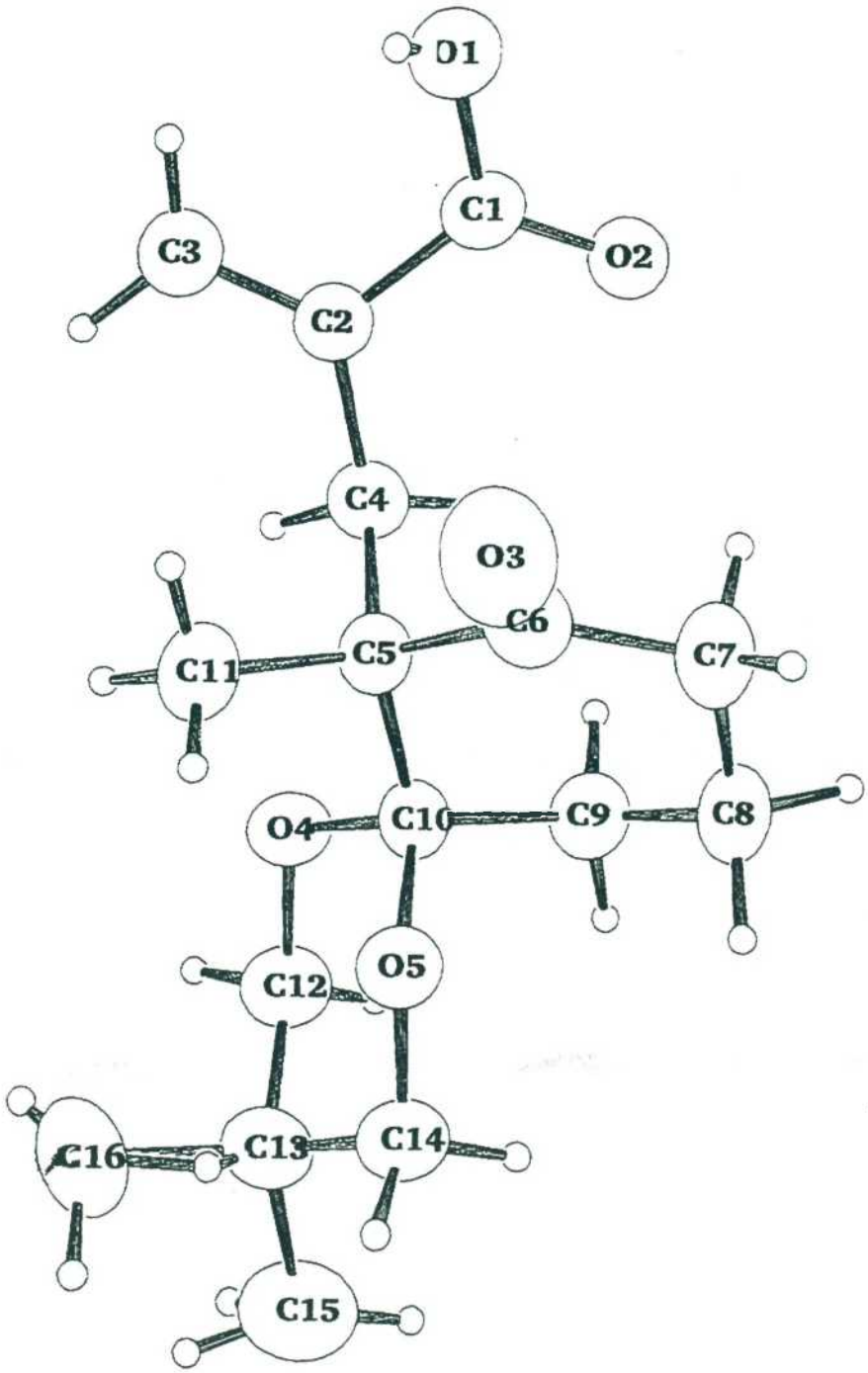


Diagram of the Molecule

BIBLIOGRAPHY

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* 97, 1345-1358.

Derissen, J.L. & Smit, P.H. (1974). *Acta Cryst.* B30, 2240-2242.

Green, M. (1968). *Rodd's Chemistry of Carbon Compounds: A Modern Comprehensive Treatise*, 2nd ed., Vol. 2, edited by S. Coffey, pp. 92-113. New York: Elsevier.

Haltwanger, C. R., Walba, D. M. & Wand, M. D. (1980). *Cryst. Struct. Commun.* 9, 1195-1200. Hall and Stewart, 1990 LATCON.

Koer, F. J., De Kok, A. L. & Romers, C. (1972).. *Rec. Trav. Chim. Pays-Bas.* 91, 691-699.

Ösawa, E. & Varnali, T. (1995). *Conformational Behavior of Six-Membered Rings: Analysis, Dynamics, and Stereoelectronic Effects*, edited by E. Jauristi, pp. 146-147. New York: VCH.

Stout, G. H. & Jensen, L. H. (1989). *X-Ray Structure Determination: A Practical Guide*, 2nd ed. New York: John Wiley & Sons.

Sutton, L. E. (1965). *Tables of International distances AD and Configurations in Molecules and Ions. Suppl.* 1956-1959 (The Chemical Society), pp. S15 and S22.